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(54) PASTE FOR OUTER CONDUCTOR OF LOW-TEMPERATURE BAKED MULTILAYER CIRCUIT SUBSTRATE

(57)Abstract:

PURPOSE: To manufacture paste for outer conductors of a low-temperature baked multilayer circuit substrate, which has migration resistance, high adhesiveness, oxidation resistance and besides excellent electric connecting to inner conductors, by specifying the concentration of silver in the surface of each of particles in the paste and the average diameter of the particles respectively.

CONSTITUTION: Paste for outer conductors of a low-temperature baked multilayer circuit substrate is represented by a general formula of Ag_xCu_{1-x}($0.01 \leq X \leq 0.4$ in atomic ratio), and it has the concentration of silver in the surface of its particle set higher than 2.1 times the average concentration of silver in the whole of each of the particles. This paste is manufactured through the process of mutually compounding 0.1 to 30 pts.wt. of glass frit, in which particles each have an average diameter of 0.1 to 10μm and also not less than 90% of them each have a diameter of not larger than 15μm, against 100 pts.wt. of copper alloy powder in which particles each having a region where the concentration of silver is gradually increased toward the surface of the particle each have an average diameter of 0.1 to 20μm and also not less than 90% of them each have a diameter of not larger than 25μm, the copper alloy powder and an organic vehicle respectively. The paste can thus have excellent adhesiveness to the substrate, solderability, migration resistance and oxidation resistance respectively.

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CLAIMS

[Claim(s)]
[Claim 1] It is expressed with a general formula Agx Cu 1-x (however, 0.01<=x<=0.4, an atomic ratio). Have the field which the silver concentration on the front face of a particle is higher than 2.1 times of average silver concentration, and silver concentration increases toward a particle front face. As opposed to the copper alloy powder 100 weight section characterized by for mean particle diameter being 0.1-20 micrometers, and powder 25 micrometers or less being 90% or more The paste for low-temperature baking multilayered circuit board outer conductors characterized by consisting of the glass frit 0.1 whose powder 15 micrometers or less it is 0.1-10 micrometers in mean particle diameter, and is 90% or more - the 30 weight sections, and an organic vehicle [claim 2] The paste for low-temperature baking multilayered circuit board outer conductors which comes to carry out 0.1-20 weight section addition of the cuprous-oxide powder whose powder 25 micrometers or less it is 0.1-20 micrometers in mean particle diameter, and is 90% or more at a paste according to claim 1 to the copper alloy powder 100 weight section.
[Claim 3] The paste for low-temperature baking multilayered circuit board outer conductors characterized by a glass frit according to claim 1 or 2 consisting of a glass frit which used as the principal component PbO, SiO2B 2O3, and one or more sorts of oxide components chosen from ZnO.
[Claim 4] The paste for low-temperature baking multilayered circuit board outer conductors according to claim 1 to 3 the conductor of a inner layer -- a circuit or a beer hall -- a conductor or a through hole -- a conductor -- at least -- silver -- The low-temperature baking multilayered circuit board which has the outer conductor expressed with the general formula Agx Cu 1-x (however, 0.01<=x<=0.4, an atomic ratio) which prints to the outer layer of the low-temperature baking multilayered circuit board characterized by being one or more sorts chosen from silver-palladium, silver-platinum, and gold, and it comes to sinter.
[Claim 5] The low-temperature baking multilayered circuit board characterized by the silver concentration of the front face of an outer conductor according to claim 4 being higher than the twice of average silver concentration.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] the low-temperature baking multilayered circuit board of this invention -- business -- an outer-conductor paste can be used as an outer conductor of the low-temperature baking multilayered circuit board which demonstrates high density and the property excellent in the high-speed transmission of a signal. Moreover, it can use as a hybrid IC circuit.
[0002]
[Description of the Prior Art] While high integration and densification progress in the electronic ingredient field in recent years, the multilayering technique is advanced also as a hybrid IC substrate. Especially, the multilayering by the low-temperature baking green sheet multilayer is advanced. As the approach of multilayering, it is a conductor to the green sheet (substrate before baking) beforehand produced by the drill or punching in the hole for a beer hall or through holes. A dielectric and resistive paste are printed further if needed, and the paste using exotic powdered metals, such as silver and silver-palladium, silver-platinum, and gold, and the printed green sheet are multilayered, and in an oxygen content ambient atmosphere or air, at 550-1060-degree-C low temperature, coincidence baking is carried out and it is used as a multilayered circuit board. Naturally, as a result of being obtained in this way, the paste of silver and silver-palladium, copper, silver-platinum, and gold has been used as an outer conductor (outer layer conductor) of a low-temperature baking multilayered circuit board. Moreover, after the inner conductor which consists of said noble metals is formed in air or an oxygenated ambient atmosphere, the method of calcinating the copper paste as an outer conductor by the inert atmosphere (for example, inside of nitrogen-gas-atmosphere mind) is also well-known.
[0003] After producing an outer conductor, if needed, printing baking is repeated, a crossover glass, exaggerated glass, and external resistance object etc. is performed, and the circuit as a low-temperature baking multilayered circuit board is formed.
[0004]
[Problem(s) to be Solved by the Invention] Until now, there are the following troubles in the well-known silver used as an outer conductor of a low-temperature baking multilayered circuit board, silver-palladium, silver-platinum, gold, and copper. That is, although the junction at the time of baking with the inner conductor (namely, silver and silver-palladium, silver-platinum, gold) of a noble-metals system is good in order to tend to build an inner conductor and the solid solution when an outer conductor is silver, although the migration nature between inner conductors does not become a problem so much since the laminating is carried out in using as an inner conductor in the case of silver, the silver migration between the outer conductors between high density patterns like a multilayered circuit board becomes a problem.
[0005] In silver-rose JIUMU, the junction at the time of baking with the inner conductor which used the noble-metals system is good too, but as an outer conductor used as a fine line, an impedance is too high and it is not suitable for a practical use circuit. In the outer conductor of silver-platinum, although the junction at the time of baking with the inner conductor of a noble-metals system is good and the solder foods crack at the time of soldering of dependability and a fine line circuit is good, a problem is in migration nature.
[0006] With money, although the junction at the time of baking with a noble-metals system inner conductor is good similarly, cost will start too much. In using copper as an outer conductor, the impedance in a fine line is also low, electrical characteristics are also excellent, but since it is calcinated and produced in an inert atmosphere after calcinating and forming the inner conductor of said noble-metals system in air or an oxygen content ambient atmosphere, the amount of addition oxygen for calcinating an organic vehicle completely must be controlled quite severely, and, generally baking in nitrogen-gas-atmosphere mind 10 ppm or less has been used. Therefore, an organic

vehicle burns, it flies, there is **, and it is easy to produce poor soldering. moreover, the case where an outer conductor is copper -- the time of baking -- the junction to said noble-metals system inner conductor (a beer hall -- a conductor and a through hole -- a conductor -- leading) -- setting -- the time of baking of copper powder, or the minute amount oxidation state of a state of preservation -- alloying with an inner conductor -- inadequate -- becoming -- easy -- electric [in a plane of composition / poor] -- a lifting -- being easy .

[0007]

[Means for Solving the Problem] This invention is expressed with a general formula Agx Cu 1-x (however, 0.01<=x<=0.4, an atomic ratio). And the silver concentration on the front face of a particle is higher than 2.1 times of average silver concentration, and the mean particle diameter which has the field which silver concentration increases toward a particle front face is 0.1-20 micrometers. And the copper alloy powder 100 weight section whose powder 20 micrometers or less is 90% or more is received. With the mean particle diameter of 0.1-10 micrometers, and the glass frit 0.1 whose powder 10 micrometers or less is 90% or more - 30 weight sections, And the paste for low-temperature baking multilayered circuit board outer conductors characterized by containing an organic vehicle, and the inner conductor (a beer hall -- a conductor --) of the inner layer which is one or more sorts chosen from silver and silver-palladium, silver-platinum, and gold in the paste of this presentation a through hole -- a conductor -- containing -- it is related with the low-temperature baking multilayered circuit board which consists of an outer conductor expressed with the general formula Agx Cu 1-x (however, 0.01<=x<=0.4, an atomic ratio) which prints to the outer layer of the low-temperature baking multilayered circuit board which it has, and it comes to sinter.

[0008] The atomizing method this invention person has already applied for the method of producing the copper alloy powder which can be used by this invention is desirable (USP No. 5091114). According to the contents of an indication, it is the approach of dissolving the copper of this presentation, and silver by the high temperature of 100 times more than 1000, atomizing and carrying out the rapid solidification of the melt in an inert gas ambient atmosphere, using high-speed inert gas, and producing impalpable powder.

[0009] A silver content x is deficient in sufficient oxidation resistance as an outer conductor at less than 0.01 at the time of baking, and junction to an inner conductor cannot be taken enough. In exceeding 0.4, the migration of the silver between outer conductors becomes easy to happen. Preferably, it is 0.01-0.35 and 0.01-0.25 are still more desirable. Moreover, although the silver concentration of the front face of the copper alloy powder which can be used by this invention is higher than average silver concentration and it has the field which silver concentration increases toward a particle front face, surface silver concentration is a thing of 2.1 times or more of average silver concentration. In the case of less than 2.1 times, junction to un-not only 10 minutes but an inner conductor does not have the enough oxidation resistance at the time of baking of a conductor. Preferably, they are 2.1 or more-time 40 or less times. Furthermore, 3 or more-time 30 or less times are desirable.

[0010] The paste for outer conductors of this invention obtains sufficient electric flow by the alloy junction at the time of baking with an inner conductor. That is, it is in being easy to alloy the noble-metals inner conductor containing the silver and silver-palladium, silver-platinum, or gold of the inner conductor already formed, and the outer-conductor paste of a presentation to cut easily, therefore sufficient electric junction being acquired from the noble-metals component of silver and said inner conductor building a complete solid solution, and silver concentration being high on the copper alloy powder front face of use by this invention. moreover -- as the outer conductor after sintering -- average silver concentration -- low -- a conductor -- it is also one of the advantages that there is also no problem of the migration of a between.

[0011] If oxidization of the copper grain child at the time of baking is also slight in it being a copper outer conductor, junction by the alloy with the inner conductor which consists of the silver of the inner conductor already formed, platinum, palladium, a golden component, etc. will not fully be performed, but a contact fault will be started. Although mean particle diameter is 0.1-20 micrometers, the amount of oxygen which the grain child who is less than 0.1 micrometers contains is high, and, as for the copper alloy powder used by this invention, it tends to wake up the defective continuity at the time of baking. the case where it exceeds 20 micrometers -- the blinding at the time of the formation of filer in -- a lifting -- easy -- desirable -- alike -- ** It is desirable and is 0.2-15 micrometers in mean particle diameter. Furthermore, existence of a particle 25 micrometers or less is required for 90% or more because of sufficient alloying with the fine line printing nature and the inner conductor like the outer conductor of a low-temperature baking multilayered circuit board. Furthermore, it is 95% or more preferably.

[0012] The mean particle diameter used by this invention expresses volume addition mean particle diameter. Using the laser diffraction mold mean-particle-diameter measuring device (Shimazu SALD1100), in ethylene glycol, measurement distributed the copper alloy particle completely and measured the solvent. Moreover, existence of powder 25 micrometers or more was similarly searched for from particle size distribution using the laser diffraction mold mean-particle-diameter measuring device.

[0013] Moreover, although the paste for low-temperature baking multilayered circuit board outer conductors of this invention is carrying out 0.1-30 weight section content of the glass frit to the copper alloy powder 100 weight section, it gives firm adhesive strength with a multilayered circuit board as a duty of a glass frit. The mean particle diameter of a glass frit is 0.1-10 micrometers. Volume addition performed measurement like copper alloy powder using the laser diffraction mold particle-size-distribution measuring device (Shimazu SALD1100). The distribution under paste is difficult in mean particle diameter being less than 0.1 micrometers, in exceeding 10 micrometers, it causes the lack of sintering, or a printability is bad and tends to sediment. Preferably, mean particle diameter is 0.2-7 micrometers. Moreover, that whose percentage of 15 micrometers or less is 90% or more can be used. The alloying by it being less than 90% with an inner conductor will be checked. Preferably, it is 99% or more.

[0014] Moreover, in there being no adhesive strength sufficient when a glass frit is under the 0.1 weight section and exceeding 30 weight sections, sintering of copper alloy powder becomes inadequate. Preferably, it is 0.2 - 20 weight section. as the component of a glass frit -- PbO, SiO2, B-2 O3, and ZnO -- since -- one or more selected sorts being used as a principal component, and as a glass frit used For example PbO-SiO2-B-2 O3 and PbO-SiO2 - ZnO and PbO-SiO2-Bn 2O3 - ZnO, PbO-SiO2-CaO, and PbO-SiO2 - BaO, PbO-SiO2-MgO, and PbO-SiO2 - MnO, PbO-B 2O3, and PbO-B2 O3-ZnO, PbO-B2 O3-CaO-ZnO, PbO-B2 O3-SiO2-CaO, PbO-B2 O3-SiO2-MgO, PbO-SiO2-aluminum 2O3, and PbO-SiO2-B-2 O3 - aluminum 2O3, PbO-B2 O3-aluminum 2O3, PbO-SiO2-aluminum2 O3-CaO, PbO-SiO2-aluminum2 O3-MgO, PbO-B2 O3-aluminum2 O3-CaO, and SiO2-B-2 O3 Amorphism nature, such as a system, Or it is desirable to use a crystalline glass frit. Especially, the glass frit containing PbO is desirable. At the time of baking, what is combined with a multilayered circuit board is desirable, as softening temperature of a glass frit, as a role of a glass frit, it is for raising an adhesive property with a low-temperature baking multilayered circuit board or the outer conductor of a presentation to cut, and 550-degree-C or less thing 200 degrees C or more is [650 degree-C or less thing 200 degrees C or more is desirable, and] still more desirable. Moreover, it is desirable that coefficient-of-thermal-expansion differences are a multilayer substrate and less than 50%.

[0015] In order to raise bond strength to the paste for outer conductors of this invention for low-temperature baking multilayered circuit boards, it is still better for it to add cuprous-oxide powder. The mean particle diameter of cuprous-oxide powder is good to use a 0.1-20-micrometer thing. In the case of less than 0.1 micrometers, the dispersibility of a under [a paste] is bad. In exceeding 20 micrometers, it checks sintering of copper alloy powder. Preferably, it is 0.1-10 micrometers. Moreover, as for cuprous-oxide powder, it is good that the percentage of powder 25 micrometers or less is 90% or more. Sintering of not only screen-stencil nature but copper alloy powder is checked as it is less than 90%. Preferably, it is 95% or more. Moreover, as an addition of a cuprous oxide, to the copper alloy powder 100 weight section, 0.1-20 weight section addition can be carried out, and it can use. In not obtaining sufficient bond strength for the case of less than 0.1 but exceeding 20 weight sections, it checks sintering of copper alloy powder. Preferably, 0.1 - 7 weight section is more desirable to 0.1 - 13 weight section and a pan. In the case of cuprous-oxide powder as well as the measuring method of copper alloy powder, volume addition performed measurement of mean particle diameter and particle size distribution. It asked for the rate of 25 micrometers or less from particle size distribution.

[0016] In addition, further, in order to raise an adhesive property with a low-temperature baking multilayered circuit board, and solder wettability, 0.1-20 weight section addition of the impalpable powder (preferably mean particle diameter of 0.01-10 micrometers), such as a cupric oxide, the bisumuth oxide, lead oxide, a magnesium oxide, a zinc oxide, oxidation boron, a silica, and cadmium oxide, can also be carried out to the copper alloy powder 100 weight section.

[0017] Although the paste for low-temperature baking multilayered circuit board outer conductors of this invention contains the organic vehicle, as an organic vehicle, there is especially no specification and it can use a well-known organic vehicle. It is the object which gives moderate viscosity and thixotropy to a paste as a role of an organic vehicle, for example, is well-known organic binders, such as ethyl cellulose, methyl cellulose, acrylic resin, and butyral resin, and is the object which gives viscosity and ****** using a solvent. A solvent also with a well-known solvent can be used.

[0018] Moreover, CHIKISO agents, such as a GAPPU ring agent (a titanium coupling agent, silane coupling agent), hydrogenation castor oil, colloidal silica, and oxidization polyethylene, and higher fatty acids (for example, stearin acid, a linolenic acid, linolic acid, a palmitic acid, etc.) and those copper salt can also be added if needed. As amount of the organic vehicle used, the 1 - 300 weight section is desirable to the copper alloy powder 100 weight section. Moreover, said additive has desirable 0.001 - 30 weight section to the copper alloy powder 100 weight section.

[0019] Although calcinating in an inert atmosphere is desirable when printing and calcinating the paste for outer conductors of this invention, as an inert atmosphere, the inside of nitrogen, an argon, hydrogen, and a helium ambient atmosphere is desirable. An especially economical field to the inside of nitrogen-gas-atmosphere mind is desirable. When calcinating in these inert atmospheres, it is desirable to calcinate by whenever [about 550-1050-degree C low-temperature], and to form a sintered compact. At this time, in order to fully burn an organic vehicle off, it is still more desirable to dope oxygen to 500-600 degrees C. For example, it is desirable to dope 1-1000 ppm. Although a resistance heating furnace can also use well-known firing furnaces, such as a near infrared ray furnace, the furnace of a firing furnace of a band-conveyor type is desirable. As firing time, although there is especially no assignment, its 120 minutes are desirable at the highest burning temperature from 3 minutes.

[0020] the outer conductor of this invention which calcinated at said temperature and was formed as a sintered compact -- setting -- a conductor -- as for surface silver concentration, what [especially] is higher than average silver concentration is desirable. The silver concentration on the front face of an outer conductor has the desirable more than twice of average silver concentration, and its 3 or more times are still more desirable. That is, since it is the temperature for sintering, sintering begins from the contact of particles from fusion of a particle. a conductor with the surface mist beam silver concentration of the outer conductor obtained high at this time -- it has a front face. However, if burning temperature exceeds 1100 degrees C, the configuration of a conductor not only collapses, but an outer conductor will fuse, fluidization will take place and equalization of silver concentration will take place. moreover -- if the amount of oxygen dopes enters too much superfluously -- a conductor -- surface copper concentration increases on the contrary.

[0021] Since the surface silver concentration of the low-temperature baking multilayered circuit board outer conductor of this invention is high, also when carrying out the coat of an external resistance object, a glass paste, and the insulating paste and heat-treating them on an outer conductor further, it has oxidation resistance, and has an advantage, like there is little electric degradation of solder wettability. Although a well-known ingredient can be used as a green sheet for low-temperature baking multilayer substrates (phase before carrying out a laminating and calcinating) which can be used by this invention Especially An alumina (aluminum 2O3), forsterite (2 MgO-SiO2), A mullite (3Al2 O3 and 2SiO2), a cordylite (2MgO, 2aluminum2 O3, and 5SiO2), CaZrO3 It considers as a principal component and they are B-2 O3 and SiO2. What [added the glass component] A beta-spodumene (Li2 O-aluminum2 O3 and 4SiO2) system, BaO-SnO2, TiO2, and B-2 O3 from -- becoming BaSn2 (BO3) a system -- BaTi(BO3)2 system, aluminum 2O3, CaO, SiO2, MgO, and B-2 O3 etc. -- from -- the becoming system, BaO and aluminum 2O3, and SiO2 The textile glass yarn which consists of an additive is desirable.

[0022] For example, PbO-SiO2-B-2 O3-CaO system glass +aluminum 2O3, CaO-aluminum2 O3-SiO3-B-2 O3 System glass +aluminum 2O3, BaO-aluminum2 O3-SiO3-B-2 O3 System glass and SiO2-B-2 O3 System glass +aluminum2 O3+CaZrO3 and SiO2 </SUB>-B-2 O3 System glass +aluminum 2O3, SiO2-B-2 O3 system glass +aluminum2 O3+2 MgO-SiO2 and 2MgO-2aluminum2 O3-5SiO2 System, ZnO-MgO-aluminum2 O3-SiO2 A system and BaSnB2 O6-BaTiB 2O3 A system and aluminum2 O3-CaO-SiO2-MgO-B 2O3 A system and BaO-SiO2-aluminum2 O3-CaO-B 2O3 A system etc. is raised. It is not the object specified especially although a 5 micrometers - about 2000 micrometers thing can be used as thickness of a green sheet.

[0023] the silver concentration of the front face of the copper alloy powder used by this invention, and the low-temperature baking multilayered circuit board of this invention -- business -- measurement of the silver concentration of the front face of the outer conductor obtained with an outer-conductor paste was performed using XPS (X-ray-photoelectron-spectroscopy analysis apparatus: XSAM800 made from KRATOS).

Measuring condition: Argon ambient atmosphere after sticking a carbon double-sided tape on a sample base, sticking so that copper alloy powder or an outer-conductor chip (not carrying out an overcoat unreserved condition) may be covered on the whole surface, and fully performing a vacuum deairing <10-8 torrMgK alpha rays 10mA of specimen current 12kV ejection include angle It measured at 90 degrees.

Etching conditions: Argon gas 3keV 10-7 torr The average of 2 times of the measured value of the repeat deed beginning was made into surface silver concentration x=Ag/(Ag+Cu) and copper concentration 1-x=Cu/(Ag+Cu) for measurement and etching 5 times by turns on the above-mentioned conditions for 5 minutes. Using ICP (RF inductive-coupling mold plasma-emission-spectrometry meter), it dissolved in concentrated nitric acid and the measured value of copper alloy powder and the silver concentration of an average of an outer conductor measured the sample, after dissolving the sample in the concentrated-nitric-acid solution.

[0024] Moreover, the migration trial measured the migration time amount when producing outer-conductor width of face of 80 micrometers, and spacing of 100 micrometers, and carrying out 50DCV seal of approval to conductor spacing among 60 degrees C and 90% relative humidity. 5 hours or more were made into fitness, and less than 5 hours was made into the defect. Moreover, the electric junction in the connection side of an inner conductor and an outer conductor was judged from the impedance measurement between the outer conductors connected with the conductor of the 2nd layer in the beer hall.

[0025] Solder wettability (soldering nature) of an outer conductor was dip(ed) for 10 seconds to 230-degree-C tin / lead eutectic solder bath, and presupposed that a wetted area is good 95% or more. Less than [it] was made into the defect. The impedance of an outer conductor was measured using 4 terminal method. An example is shown below.

[0026]

[Example]

[0027]

[The example 1 of powder production] 571.5g of copper grain children and 108g of silver granule children were fully mixed, and the heating dissolution was carried out to 1700 degrees C among nitrogen-gas-atmosphere mind in the graphite crucible. Melt is blown off from a crucible tip in nitrogen-gas-atmosphere mind, and it is 50kg/cm2 to jet and coincidence. To melt, it blew off and nitrogen gas was atomized. The obtained powder was 12 micrometers in mean particle diameter. the silver concentration of the front face of copper alloy powder -- 0.5, 0.4, 0.3, and 0. -- it was 2 and 0.14 and surface silver concentration was 0.45. Moreover, the average silver concentration x was 0.1 and surface silver concentration was 4.5 times the average silver concentration.

[0028] The example of production of the copper alloy powder produced like below is shown.

[0029]

[Table 1]

粉末作製例	2	3	4	5
平均銀濃度	0.2	0.25	0.05	0.12
平均銅濃度	0.8	0.75	0.95	0.88
アトマイズガス	窒素	窒素	ｱﾙｺﾞﾝ	ﾍﾘｳﾑ
ガス圧力（kg/cm^2）	50	45	60	70
平均粒子径（μm）	12	10	11	9
表面銀濃度	0.8	0.86	0.45	0.67
表面／平均銀比	4	3.44	9	5.58

[0030]

[Example 1] Powder 10 micrometers or less was classified in the copper alloy powder obtained in the example 1 of powder production. The obtained powder was 4.5 micrometers in mean particle diameter. 10g of the powder, and PbO-B2 O3-ZnO-SiO2 Glass frit (mean-particle-diameter [of 5 micrometers], 99% or more 10 micrometers or less) 0.2g, ethyl cellulose 0.05g, 0.5g [of acrylic resin], and TERUPE Norian 1g, butyl carbitol 2g, butyl carbitol acetate 2g, 0.1g [of copper I oxide powder] (mean particle diameter of 2 micrometers), and silicone oil 0.001g and 0.0001g of titanium coupling agents were mixed, and it considered as the paste.

[0031] Moreover, a silver paste, a dielectric, and ruthenium system resistive paste were printed as a circuit to the green sheet which comes to add B-2 O3, CaO, and MgO to a mullite, the laminating was carried out to ten layers, and it calcinated among 60-minute interspace mind at 800 more degrees C. On the obtained multilayered circuit board, the paste of said presentation was printed as an outer conductor. It calcinated for 10 minutes in nitrogen-gas-atmosphere mind at 700 degrees C after printing. At this time, it doped 400 ppm of oxygen to 500 degrees C.

[0032] the place which measured the silver concentration of the front face of the obtained conductor -- a front face -- silver concentration -- 0.6, 0.5, 0.45, and 0. -- it was 4 and 0.3, and surface silver concentration was 0.55 and was 2.75 times the average silver concentration. The conductivity of a conductor had the good junction to a surface outer conductor and an inner conductor, and the rise of resistance was hardly seen in the plane of composition in the interior and the exterior.

[0033] furthermore -- as a printing resistor -- a lanthanum -- a bora -- the id -- the resistor of a system -- a conductor -- it printed in between and calcinated in nitrogen-gas-atmosphere mind at 900 degrees C. the conductor of resistance -- the resistance rise by the electrode was not seen. moreover -- even if it prints overcoat glass and processes in 550-degree-C nitrogen-gas-atmosphere mind -- a conductor -- surface discoloration was not seen. It was good when the migration trial was carried out. Moreover, the impedance of an outer conductor was also good.

[0034]

[Example 2] Powder 5 micrometers or less was classified in the copper alloy powder obtained in the example 1 of powder production. The obtained powder was 2 micrometers in mean particle diameter. 10g [of obtained classification powder] and PbO-B2 O3-ZnO glass frit (mean-particle-diameter [of 0.3 micrometers, 99% or more 15 micrometers or less) 0.3g, 0.1g / of copper I oxide powder / (mean particle diameter of 0.2 micrometers), and ethyl cellulose 0.02g, 0.04g / of acrylic resin, and butyl carbitol acetate 0.6g, 0.1g (mean particle diameter of 0.2 micrometers, 99% or more 10 micrometers or less) of copper I oxide powder, and 0.001g of sedimentation inhibitors be fully mixed, and it considered as the paste

[0035] Independently, they are B-2 O3 and SiO2 to forsterite. The silver-palladium 5% paste was printed to the green sheet in which the beer hall which it comes to add was formed, further, the ruthenium system resistor was printed, the dielectric glass paste was printed, silver-palladium conductive paste was printed also in the beer hall, the six-sheet laminating of the green sheet produced similarly was carried out, and coincidence baking was carried out in air at 700 degrees C.

[0036] already -- the beer hall for connection with an outer conductor -- silver-palladium -- circuit printing was carried out, using the paste of said presentation as an outer conductor of a multilayered circuit board with which the conductor is formed. It calcinated in 10 minutes in 750-degree-C nitrogen-gas-atmosphere mind after printing. 500 ppm of oxygen were doped to 550 degrees C. the silver concentration of the front face of the obtained outer conductor -- 0.9, 0.8, 0.7, and 0. -- it was 5 and 0.4, and surface silver concentration was 0.85 and was 3.4 times the average silver concentration.

[0037] In this way, the junction to the outer conductor and inner conductor which were obtained was good, and resistance was not seen increase conductivity in a plane of composition. Moreover, the result of a migration trial was good. furthermore, a lanthanum -- a bora -- the id -- the coat of system resistive paste and the dielectric glass paste was carried out, and it calcinated in nitrogen-gas-atmosphere mind. The change in resistance in junction to a resistor and an outer conductor was as good as 0.1% or less.

[0038]

[Example 3] Powder 2 micrometers or less was classified in the copper alloy powder obtained in the example 3 of powder production. The obtained classification powder was 0.8 micrometers (99% or more 20 micrometers or less) in mean particle diameter. 10g [of classification powder], and PbO-SiO2-MgO-B2 O3-ZnO glass frit (mean-particle-diameter [of 1 micrometer], 99% or more 15 micrometers or less) 0.02g, butyl-cellosolve 0.2g, butyl carbitol acetate 0.1g, silicone oil 0.001g, and a CHIKISO agent -- 0.0001g, 0.8g (mean particle diameter of 0.2 micrometers, 99% or more 25m or less) of cuprous-oxide powder, 0.1g of cadmium oxide, and 0.1g (mean particle diameter of 0.5 micrometers, 99% or more 25 micrometers or less) of bisumuth oxide. 0.1g of palmitic acids and 0.1g of stearin acid were mixed, and it considered as the paste.

[0039] Independently, it is B-2 O3 to an alumina and a cordylite. It comes to add. The silver-platinum paste was used for the green sheet by which beer hall formation was carried out, and the circuit was formed. Furthermore, after printing ruthenium system resistive paste and a dielectric paste and printing a silver-platinum paste also in a beer hall, the eight-layer laminating of the green sheet was carried out similarly, and coincidence baking was carried out in 800-degree-C air.

[0040] the obtained multilayered circuit board -- the beer hall as an object for connection with an outer conductor -- after forming a conductor, circuit printing formation was carried out using the paste for outer conductors of said presentation. Furthermore, it calcinated for 10 minutes in 700-degree-C nitrogen-gas-atmosphere mind. At this time, it doped 300 ppm of oxygen to 500 degrees C. the place which measured the silver concentration of the front face of the obtained outer conductor -- a front face -- silver concentration -- 0.88, 0.8, 0.7, and 0. -- it was 6 and 0.5 and surface silver concentration was 0.84. Average silver concentration was 0.25 and surface silver concentration was 3.3 times the average silver concentration.

[0041] The junction to an outer conductor and an inner conductor is good, and the rise of the resistance in a plane of composition was not seen. Moreover, the result of a migration trial was good. Further, the insulating glass paste was printed to the outer conductor, and it calcinated in 550-degree-C nitrogen-gas-atmosphere mind to it. At this time, 100 ppm of oxygen were doped to 500 degrees C. The discoloration by the glass coat of the obtained outer-conductor circuit etc. was not seen.

[0042]

[Example 4] Powder 3 micrometers or less was classified in the copper alloy powder obtained in the example 4 of powder production. The obtained powder was an average of 1.2 micrometers. 10g of classification powder, and PbO-SiO2-CaO-ZnO-B 2O3 Glass frit (the mean particle diameter of 0.5 micrometers) 99% or more of 1g and 0.1g of oxidization copper 15 micrometers or less, 0.002g of bisumuth oxide, 0.025g (mean particle diameter of 0.2 micrometers, 99% or more 15 micrometers or less) of cuprous oxides, Ethyl cellulose 0.2g, 0.2g of acrylic resin, 0.1g of

butyral resin, 0.0001g of stearin acid, CHIKISO agent 0.0002g, butyl carbitol acetate 0.5g, and alpha-TERUPE Norian 0.5g are fully mixed. It considered as the paste.
[0043] another -- beta-SUPONJUMEN and BaO-aluminum2 O3-SiO2 the green sheet which consists of glass and with which the beer hall is already formed -- a conductor -- it considered as the circuit and the golden paste was printed. Furthermore, beer hall printing and after carrying out ruthenium system resistive paste printing, the six green sheet laminating produced similarly was carried out, and coincidence baking was carried out in 750-degree-C air.
[0044] the obtained multilayered circuit board -- the beer hall for junction of an outer conductor and an inner conductor -- a conductor -- after forming, circuit printing was carried out, using the paste of said presentation as an outer conductor. Furthermore, it calcinated for 10 minutes in 700-degree-C nitrogen-gas-atmosphere mind. At this time, it doped 100 ppm of oxygen to 550 degrees C. The increment in resistance in the plane of composition of an inner conductor and an outer conductor was not seen. Moreover, the migration trial was good.
[0045] the silver concentration of the front face of an outer conductor -- a front face -- 0.3, 0.25, 0.24, and 0. -- it was 2 and 0.15, and surface silver concentration was 0.275 and was 5.5 times the average silver concentration.
[0046]
[Comparative Example(s)]
[0047]
[The example 1 of a comparison] 63.5g of copper grain children and 108g of silver granule children were mixed, it put into the graphite crucible, and the heating dissolution was carried out in nitrogen-gas-atmosphere mind to .700 degree C. Melt was blown off from the crucible tip into nitrogen-gas-atmosphere mind, and 40kg/cm2 of nitrogen gas of G was blown off and atomized to melt to jet and coincidence. The obtained powder was 13 micrometers in mean particle diameter. 0.5 and the average copper concentration of the average silver concentration x were 0.5. Powder 10 micrometers or less was classified in the obtained copper alloy powder. The mean particle diameter of the powder after classification was 5 micrometers. 10g of copper alloy powder after classification, and PbO-B2 O3-SiO2 Glass (mean particle diameter of 1 micrometer) frit 0.2g, 0.01g [of copper I oxide powder] (mean-particle-diameter [of 0.5 micrometers], 99% or more 10 micrometers or less), and ethyl cellulose 0.3g, TERUPE Norian 0.6g, butyl carbitol acetate 0.3g, and 0.001g of sedimentation inhibitors were fully mixed, and it considered as the paste.
[0048] They are an alumina and BaO-B2 O3-SiO2 about a silver-platinum (3wt%) paste. It printed on the green sheet which consists of glass and by which beer hall formation was already carried out. Furthermore, after printing also in a beer hall, the well-known ruthenium system resistor was printed, and further, after carrying out the six-sheet laminating of the green sheet similarly printed after also printing a dielectric and carrying out thermocompression bonding with a hotpress, it calcinated for 10 minutes in air at 700 degrees C. As an outer conductor of a low-temperature baking multilayered circuit board with which the silver-platinum paste was similarly produced by the beer hall for connection with an outer conductor, said produced copper alloy paste was printed as a circuit. the still better known lanthanum after calcinating for 10 minutes in 900-degree-C nitrogen-gas-atmosphere mind (it doped 3000 ppm of oxygen to 500 degrees C) -- a bora -- the id -- after printing the resistor of a system, 900 degrees C was calcinated for 10 minutes.
[0049] Migration was remarkable, when it calcinated and the migration trial of the produced outer conductor was carried out. moreover, the silver concentration of the front face of an outer conductor -- a front face -- 0.1, 0.2, 0.3, and 0. -- it was 4 and 0.5, and surface silver concentration was 0.15 and was as lower as 0.3 times than average silver concentration.
[0050]
[The example 2 of a comparison] 10g [of commercial copper grain children] (mean particle diameter of 2 micrometers), PbO-CaO-SiO2-B-2O31(mean particle diameter of 1 micrometer) g, 0.1g [of acrylic resin], and TERUPE Norian 0.1g, butyl-cellosolve 0.3g, butyl rib torr acetate 0.5g, 0.2g of cupric oxides, and 0.0002g of titanium coupling agents were fully mixed, and it considered as the paste.
[0051] The paste produced on the low-temperature baking multilayered circuit board produced in the example 1 of a comparison was printed as an outer conductor. It calcinated for 10 minutes in 600-degree-C nitrogen-gas-atmosphere mind after printing (it doped 100 ppm of oxygen to 500 degrees C). The junction to an outer conductor and an inner conductor was not so good, and the increment in resistance was seen. furthermore, a lanthanum -- a bora -- the id -- the system resistor was printed and it calcinated for 10 minutes at 900 degrees C in nitrogen-gas-atmosphere mind. The matching nature with a resistor was bad and its noise was high. Moreover, the soldering nature of an external conductor was bad.
[0052]
[The example 3 of a comparison] 254g of copper grain children and 108g of silver granule children were mixed, it put into the graphite crucible, and the heating dissolution was carried out to 1700 degrees C in nitrogen-gas-atmosphere

mind. Melt was blown off from the crucible tip into nitrogen-gas-atmosphere mind, and 5kg/cm2 of nitrogen gas of G was blown off and atomized to melt to jet and coincidence. The obtained copper alloy powder was 35 micrometers in mean particle diameter.

[0053] 0.2 and the average copper presentation of the silver presentation x of an average of copper alloy powder were 0.8. surface silver concentration -- a front face -- 0.8, 0.76, 0.7, and 0. -- it was 6 and 0.5 and surface silver concentration was 0.78. Surface silver concentration was 3.9 times the average silver concentration. 10g (mean particle diameter of 35 micrometers, 30% 25 micrometers or less) of obtained copper alloy powder, PbO-B2 O3-SiO20.3(mean particle diameter of 1 micrometer) g, TERUPE Norian 0.2g, butyl-cellosolve 0.2g, 0.5g (mean particle diameter of 1 micrometer, 99% or more 10 micrometers or less) of copper I oxide, and 0.003g of titanium coupling agents were fully mixed, and it considered as the paste.

[0054] An alumina and BaO-aluminum2 O3-SiO2 After printed the golden paste to the green sheet which consists of glass and by which beer hall formation was carried out, printing the golden paste also in the beer hall, also printing the well-known ruthenium system resistor, carrying out the six-sheet laminating of the green sheet produced similarly and carrying out thermocompression bonding with a hotpress, it calcinated for 60 minutes in 700-degree-C air. the inside of the beer hall for connection with an outer conductor -- the same -- carrying out -- gold -- after producing a conductor, on the obtained low-temperature baking multilayered circuit board, said paste was used and circuit printing was carried out. It calcinated in nitrogen-gas-atmosphere mind for 600-degree-C 10 minutes after printing (300 ppm dope of oxygen to 500 degrees C).

[0055] Mean particle diameter was large, sufficient degree of sintering was not acquired but the resistance of the outer conductor was high. Moreover, the junction to an inner conductor was bad and resistance increased it remarkably. Moreover, solder wettability was also bad.

[0056]

[The example 4 of a comparison] It is powder (the average silver concentration 0.12 and the mean particle diameter of 4.5 micrometers) 10 micrometers or less in the copper alloy powder produced in the example 5 of powder production. 25-micrometeror less 99%or more 10g and PbO-B2O3-SiO2 Glass frit (the mean particle diameter of 10 micrometers) 15 micrometers or less 60% of 1g and 0.001g (mean-particle-diameter [of 0.5 micrometers], 99% or more 25 micrometers or less) of copper I oxide powder, and ethyl cellulose 0.3g and TERUPE Norian 3g are mixed. It considered as the paste. The paste produced as an outer conductor of the same low-temperature baking multilayered circuit board as the example 3 of a comparison was printed. Furthermore, it calcinated in nitrogen-gas-atmosphere mind for 600-degree-C 10 minutes (it doped 300 ppm of oxygen to 500 degrees C). Sufficient degree of sintering was not acquired but the resistance of an outer conductor was high. Moreover, the resistance in a plane of composition with an inner conductor was very high. However, migration was good. Moreover, solder wettability was bad.

[0057]

[The example 5 of a comparison] The copper alloy powder obtained in the example 1 of powder production was classified by 10 micrometers. The powder after the obtained classification was 4.5 micrometers (99% or more 25 micrometers or less) in mean particle diameter. 10g [of powder after classification] and PbO-SiO2-ZnO (mean-particle-diameter [of 30 micrometers], 10% 15 micrometers or less) glass frit 0.3g, ethyl cellulose 0.5g, and TERUPE Norian 1g were fully mixed, and it considered as the paste.

[0058] forsterite and B-2 O3 from -- the silver-palladium paste was printed on the becoming green sheet by which beer hall formation was carried out. After printing a silver-palladium paste also in a beer hall, the six-sheet laminating of the green sheet produced similarly was carried out, and thermocompression bonding was carried out by hot braces. Furthermore, heating baking was carried out for 800-degree-C 60 minutes. the beer hall for outer conductors of the obtained multilayered circuit board -- the same -- carrying out -- silver-palladium -- after forming a conductor, said paste was printed as an outer conductor. It calcinated for 10 minutes in 700-degree-C nitrogen-gas-atmosphere mind after printing. (900 ppm dope of oxygen to 500 degrees C) . the obtained copper alloy -- a conductor -- a glass frit -- a conductor -- depositing in the film, resistance was high. moreover, the silver concentration of the front face of an outer conductor -- 0.15, 0.18, 0.2, and 0. -- it was 2 and 0.2 and surface silver concentration was lower than average silver concentration at 0.165.

[0059]

[The example 6 of a comparison] The copper alloy powder obtained in the example 1 of powder production was classified by 10 micrometers. The obtained classification powder was an average of 4.5 micrometers. 10g of powder after classification, and PbO-SiO2-B-2 O3 Glass (mean particle diameter of 1 micrometer) frit 5g, ethyl cellulose 0.3g, TERUPE Norian 1g, and 0.002g of titanium coupling agents were fully mixed, and it considered as the paste.

[0060] BaO-aluminum2 O3-SiO2 The circuit and the beer hall printed the silver paste to the green sheet which consists of glass and with which the beer hall is formed beforehand. Furthermore, ruthenium system resistive paste was printed, thermocompression bonding of the six green sheets produced similarly was carried out, and they were calcinated in 700-degree-C air for 1 hour. furthermore, the inside of the beer hall for connection with an outer conductor -- the same -- carrying out -- silver -- after forming a conductor, said copper alloy paste was printed. Heating baking was carried out for 10 minutes in 600-degree-C nitrogen-gas-atmosphere mind after printing (it doped 400 ppm of oxygen to 500 degrees C). Glass deposited on the front face and, as for the outer conductor after baking, sufficient conductivity was not acquired in a plane of composition with an inner conductor.

[0061]

[The example 7 of a comparison] The copper alloy powder obtained in the example 1 of powder production was classified by 10 micrometers. The obtained classification powder was 4.5 micrometers in mean particle diameter. 10g [of powder after classification] (mean-particle-diameter [of 4.5 micrometers], 99% 25 micrometers or less) and ethyl cellulose 0.3g, TERUPE Norian 0.4g, and butyl carbitol acetate 0.3g were fully mixed, and it considered as the paste.

[0062] It screen-stenciled as an outer conductor of the multilayered circuit board produced in the example 6 of a comparison. Heating baking was carried out for 10 minutes in 600-degree-C nitrogen-gas-atmosphere mind after printing (400 ppm dope of oxygen to 500 degrees C). the copper alloy after baking -- the adhesive strength with a multilayer substrate was insufficient for the conductor, and it separated simply from the substrate.

[0063]

[The example 8 of a comparison] 10g [of powder 10 micrometers or less] (mean-particle-diameter [of 4.5 micrometers], 99% or more of powder 25 micrometers or less) and PbO-B2 O3-SiO2 glass frit (mean-particle-diameter [of 1 micrometer], 99% or more 15 micrometers or less) 4g, 3g [of copper I oxide] (mean-particle-diameter [of 18 micrometers, 70% 25 micrometers or less), and ethyl cellulose 0.7g, butyl carbitol acetate 2g, and 0.001g of sedimentation inhibitors be fully mixed in the copper alloy powder obtained in the example 1 of powder production. It considered as the paste. The obtained paste was screen-stenciled as an outer conductor of the same multilayered circuit board as the example 7 of a comparison. Heating baking was carried out for 800-degree-C 30 minutes after printing. (100 ppm dope of oxygen to 500 degrees C) . the copper alloy after baking -- sintering of a conductor is insufficient and sufficient conductivity in a plane of composition with an inner conductor was not acquired.

[0064]

[Effect of the Invention] This invention is expressed with a general formula Agx Cu 1-x (0.01<=x<=0.4, atomic ratio). The silver concentration on the front face of a particle is higher than 2.1 times of average silver concentration. Are 0.1-20 micrometers in mean particle diameter which has the field which silver concentration increases toward a particle front face, and 20 micrometers or less receive 90% or more of copper alloy powder 100 weight section. Although the paste for outer conductors of a low-temperature baking multilayered circuit board with which 15 micrometers or less consist of 90% or more of the glass frit 0.2 - 30 weight sections, and organic vehicles with the mean particle diameter of 0.1-10 micrometers is offered In order to alloy easily at the time of the inner conductor which consists of silver, silver palladium, gold, and silver-platinum, and baking it not only to to have the outstanding adhesive property with a substrate, solder wettability, migration-proof nature, and oxidation resistance, but The outer conductor and low-temperature baking multilayered circuit board which have the outstanding electric junction nature are offered.

[Translation done.]